

1. Introduction

The main goal of the project was to contribute to the further development of Scanning Electrochemical Microscopy (SECM). Working out new measuring tips, improvements in hardware units and in measuring protocol were planned to broaden the application field of this method invented by A.J. Bard in the last part of the twentieth century. Originally the adaptation of SECM for micro-scale corrosion studies and using the improved method for studying special corrosion processes has been proposed.

The initial SECM measurements employed amperometric detection and platinum disc microelectrode measuring tip. Up till now the overwhelming majority of the measurements have still been done with this option. It is expected however, that with ion-selective microelectrodes detailed information could be obtained about steps of certain reactions proceeding at microenvironments. Unfortunately the early attempts turned up serious problems in cases when ultramicro size ion-selective electrodes were used as measuring tip in SECM. These problems not affecting seriously the potentiometric measurements of conventional analytical chemistry are the following:

- interaction of electric field with the potentiometric signal.**
- exposition time dependence of selectivity,**
- slow response of potentiometric measuring method.**

In our studies carried out in the framework of the project top priority was given for increasing the potential of ion-selective potentiometric measurements in SECM. The above mentioned problems were investigated. The results helped to learn the magnitude of the difficulties and could give help to do the necessary changes.

In other part of the work new measuring tips, new units were developed and used for studying different problems employing SECM methods.

2. Short introduction of main results obtained in the project.

2.1. Results obtained studying special problems in potentiometric SECM

2.1.1. Studies of electric field interaction on the potentiometric SECM.

When potentiometric measurements are carried on in living tissues for measuring concentration of different ionic species the local changes of electric potential generated by natural physiologic processes would interfere with the analytical signal. In order to minimize this special measures are generally taken in life science experiments. In early works studying corrosion processes with potentiometric SECM however, no care was taken to avoid possible field potential interactions. In some cases from SECM signals unrealistic local concentration values could be guessed. It was obvious that local electric field generated by ongoing reactions as part of the locally measured potentiometric signal could be responsible for those errors. Therefore in our studies the extent of influence of field potential in potentiometric SECM measurements has been investigated¹ in details as well as method for minimizing the influence were worked out². In these studies special epoxy embedded bimetallic samples-, different ultramicro ion-selective electrodes-, scanned open pipette reference microelectrodes were employed. Multi barrel measuring tips containing the reference barrel were worked out to minimize the electric field between the measuring and reference electrode and used in corrosion studies with SECM. The financial support of the project allowed us to purchase a new micropipette puller that could be used for twisted multi barrel micro tip fabrication. Several reports have been published in international journals, presented in meetings and a well-defended BSc. thesis has been written about the results of these studies.

2.1.2 Investigation of exposition time dependence of selectivity

Selectivity of ion-selective electrodes is an important parameter showing how far the concentration of certain interfering ions can be tolerated without disturbing the measurements of the other-, so called own ion concentration. Usually these parameters are determined experimentally for equilibrium conditions. This means that the cell potential is followed in time and the steady values are taken. Similarly, in potentiometric methods of analytical chemistry the steady potential values are used for calibration and for sample measurements. It was indicated³ that small concentration of interfering ions having no influence on the steady potential can still affect the potential – time transient following fast solution changes. In SECM the measuring tip travels step by step from one sampling spots to the next one. Therefore if electrode potential data are taken at very short time after steps, then even the low level presence of interfering ions can bring in distortion of SECM images. In our experiments, this short-term influence of interfering ion activity change on ion-selective micropipette electrode potential has been studied in the first time⁴. We showed that a change in the activity of interfering ions can result in a short-term electrode potential transient that should be taken into consideration in parameter setting for SECM measurements. The activity step method was employed, using NH_4^+ ion-measuring micropipettes. Solutions containing equal concentrations of NH_4^+ ions with or without K^+ ions were rapidly introduced and the short-term change in electrode potential was recorded. Rapid overshooting transient potential signals appeared following the K^+ activity step in the range where the interfering K^+ did not affect the long-term electrode potential. In corrosion studies imaging the local activities of Zn^{2+} and Cu^{2+} ions in presence of corrosive NaCl solution must be care taken to select the right timing of the tip travel. The results were presented in scientific meetings and described in Ph.D. thesis of Daniel Filotás.

2.1.3. Efforts for increasing the scanning rates in potentiometric SECM

In other probe microscopies like in STM or in AFM the needed scanning time ranges from sub seconds to tens of the seconds. Unfortunately, in potentiometric SECM much longer times are needed for obtaining chemical images about different samples. The time needed for the so called open circuit potential measurements with the available instruments limits the shortening of applicable scanning time. The higher is the resistance (R) of the measuring probe and the capacity of the measuring circuit (C) the higher time is needed for obtaining reliable potential value reflecting the activity of the ionic species to be detected. We fabricated and used in our studies antimony or tungsten micro disc electrodes for pH measurements. Their resistance is relatively small. Their other advantage is that they can be used also in amperometric mode making feasible the feedback effect based tip - surface distance adjustment. For selective detection of other ions we used micropipette type ion-selective probes. Their advantage is that the same procedure can be employed for preparation of sensors for detecting different ions. For ion measurements of certain ion just the right selective ion detecting cocktail has to be employed. Micropipette electrodes easily can be fabricated with different tip sizes. Their resistance however, is very high especially that of their ultramicro versions.

In our earlier studies⁵ solid contact micro pipette electrode form was worked out for decreasing substantially the resistance. The electrodes were proved well applicable in potentiometric SECM and showed highly extended life times. In the recent project work⁶ a further developed version of the solid contact micropipette electrodes were prepared and used. Double barrel tips having Zn^{2+} and pH detecting sensors, solid contact Zn^{2+} and Cu^{2+} measuring pipettes were prepared, tested and used. The working program of our home made SECM apparatus has been modified for saving scanning time. On one hand the multi barrel tips and the new working program allowed simultaneous imaging with the two sensors. On the other one, experiments were carried out for decreasing the number of necessary sampling spots trying to adjust the tip travel track to the symmetry, size and shape of the sample surface. If scanning without long enough waiting period of the tip at each sampling spot was employed, then a distorted image could be created from the collected data. In other experiments the distortions of the chemical images caused by the too short sampling periods in potentiometric SECM was investigated. Since the distortion was resulted by the convolution of time constant of the measuring system with the local ion activity change, therefore it was expected that the local ion activity values could be obtained by bringing the data field through a deconvolution algorithm. Based on the studies it was concluded that upon guessing well the RC value of the measuring system the distorted images could be dramatically improved.

Double barrel SECM measuring tip having Zn^{2+} and Cu^{2+} ion-selective micropipettes with non-ideal selectivity was used for corrosion measurements. From the two electrode potential values taken with the two sensing elements at certain location the local activity of the different ions could be determined using the Nicolsky equation.

2.2. Results obtained investigating details of certain corrosion reactions

2.2.1. Ti alloys

Titanium or titanium alloys containing dental implants are very often employed surgical component used for supporting missing or extracted teeth or dentures. It has been generally accepted that instantaneously evolving, compact TiO_2 layer coats their surface. It avoids corrosion and releasing unwanted ions from them. We investigated the kinetics and nature of the reaction resulting formation of that passive layer. In those studies the implants were embedded in epoxy resin. Their surface was polished and could be easily renewed. At different times after surface renewing SECM approach curves were made using ferrocene-methanol redox mediator. The change of SECM feedback character after exposing the surface to buffered electrolyte solution could be used for estimation the growing rate of the passive film. Similarly open potential measurements, impedance spectroscopic studies as well as local oxygen concentration reporting SECM line scans were carried out in different times after surface polishing. All these experiments clearly proved that the formation of TiO_2 surface film is a timely process^{7,8}. If the surface film gets mechanically damaged - let say – during implantation, then the self-healing of it takes several minutes. The results gave also some information about details of the steps of self-healing process. During that time ions are formed and can get into the surrounding living tissues.

It was also important to now, how electric polarization influences the character of the passive layer. The change of character of TiO_2 surface layer upon electrochemical polarization has been investigated using SECM and impedance spectroscopy in our studies. Quantitative information on the electron transfer rates (k_{eff}) at the titanium surface was obtained using the feedback operation of SECM with ferrocene-methanol (FcMeOH) as electrochemical mediator. An increase of k_{eff} values with the increase of the negative polarization was detected, a feature that correlates well with the decrease of titanium oxide resistance with increasing cathodic polarization observed using electrochemical impedance spectroscopy (EIS). In addition, SECM operation in the redox competition mode proved that hydrogen was absorbed in the surface oxide film leading to changes in conductivity and electrochemical reactivity. It was proved that the passive protective film can get a more conductive oxide structure when it is exposed to high polarization potential⁹. This may decrease the anticorrosion character and can decrease the viability of the cells of the surrounding living tissue when the object is implanted.

Nitinol is a titanium alloy that contains 50% nickel. It is used extensively in dentistry. In the frame work of the project the effect of anodic polarization¹⁰ and the exposition of slightly acidic media on the stability of the protective surface layer was studied using SECM, atomic absorption spectroscopic (AAS) and other, conventional methods. It was observed that when the nitinol was exposed to slightly acidic medium, it loosed the protective surface film originally formed on its surface in ambient conditions. During this considerable amount of health hazardous nickel species discharged from the nitinol as it was proved by AAS. Interestingly by the exposition time the self-healing of the protecting film could be observed¹¹. Slight acidity can develop in living tissue that surrounds certain medical device made of nitinol. Therefore the release of nickel ions before compact passive film formation in self-healing reaction cannot be outlined. After the application of an anodic polarization treatment to nitinol, due to passive layer breakdown a heterogeneous distribution of anodic and cathodic reaction sites was observed to develop extending over different active areas on the surface of the material.

3D printing technology is getting popular in producing biomedical implants. Its advantage is obvious when objects with individual shape and size is needed for implanting. CMT (Cold Metal Transfer) type 3D printing technology can be used for preparation Ti alloy implantable object. Owing to the special characteristics of the melting/cooling steps it was expected that the corrosion resistance of the 3D printed Ti alloy objects some extent differs from the ones of prepared with conventional

technologies. Participating colleague Zoltán Meiszterics worked also in a team dealing with developing 3D printing technology for Ti alloy implant preparation. In our work the corrosion resistance of 3D printed TiAl6V4 alloy samples have been studied using scanning electrochemical microscopy (SECM) and other conventional electrochemical methods. The action and stability of the spontaneously forming TiO₂ protective layer on this sample have been investigated. Furthermore, the formation rate of it has been measured. The results have been presented in Matrafűred 2021 International conference on Chemical sensors. A paper was submitted to the international journal of Electroanalysis for publication

In our work the corrosion properties of different Ti alloy medical implants have been investigated in details with advanced methods. The results seriously proved that the formation of passive surface layer at ambient conditions is not an instantaneous process as it generally believed. Its complete formation can be as long as 20-30 minutes. During this time implanted metal surface can release health hazard ions into their living environment. Similarly electrochemical polarization can weaken the passive character. Therefore care must be taken to avoid mechanic damage or electrochemical polarization of titanium alloy implants. Our results were published in journals dealing with electrochemical research. It was suggested however, that these important findings need to be disseminated for broader scientific audiences. Therefore a paper has been written and submitted into a journal of broader scope¹². In that paper we showed how long time it needs for self-healing of the passive layer after mechanic damage or other kind of brake down. We discussed what kind of chemical reaction, pH change and metal ion releases of cytotoxic nature can occur during self-healing of the titanium implants implanted into living environment.

2.2.3. 3D printed Al alloy

Owing to its excellent corrosion resistance, highest strength among non-heat treatable Al alloys, high ductility and good weldability AlMg4.5Mn0.7 (5083 aluminum) alloy is a popular material in different industrial applications. Cooperating research group worked out experimental CMT (Cold Metal Transfer) type 3D technology for preparing objects from this alloy. In our experiments¹³ the corrosion behavior of the material made with 3D and with conventional technology was compared. Tafel plots, open circuit potential-time function, atom absorption spectroscopy (AAS) and SECM measurements detecting local surface activity with feedback measurements, making pH and oxygen detecting line scans were made. The corrosion resistance of the printed plate was found higher than that of the conventionally made Al alloy. The corrosive electrolyte caused a visible pitting corrosion on the base material, this was not observable on the 3D printed material. The beneficial character was most likely resulted by the fast cooling rate in 3D technology where special microstructure was formed.

2.2.4. Investigation of the cytotoxic effect of Ti-Mg coupling

In case of galvanically coupled Ti-Mg particles cytotoxic effects were observed in case of different cells. The anodic Mg side was guessed having the major role, but some possible effect of titanium in the cytotoxic mechanism of galvanically coupled these two could not be completely discarded. In our previous work we dealt with corrosion properties of Mg and Ti alloys. May be this made our international researcher colleagues to ask us to take part in the work trying to find the responsible mechanism. In our recent work, cooperating with them, that possible role was examined. A model galvanic cell (MGC) was prepared to simulate the Mg–Ti particles. The electrochemical reactivity of the Ti sample and the pH change in it due to galvanic coupling with Mg were investigated using scanning electrochemical microscopy (SECM). It was observed that the Ti surface changed from passive to electrochemically active when coupled with Mg. Furthermore, after only 15 min of galvanic coupling with Mg, the pH in the electrolyte volume adjacent to the Ti surface increased to an alkaline pH value. It was shown that the viability of Hs27 cells significantly diminished when Mg and Ti were galvanically coupled compared to when the two metals were electrically disconnected. It was concluded that the coupling Mg particles to Ti resulted in seizing the passive character of the Ti surface. During coupling certain chemical processes proceed at the

activated metal/electrolyte interface. The products of these can contribute to the cytotoxic effects of galvanically coupled Ti–Mg particles. About the results a detailed paper has been published¹⁴

2.2.5. Investigation of corrosion of Mg alloys

Magnesium and its alloys are broad scale used in different area. In certain cases the alloys are used just as self-sacrificing anti-corrosion utensil. Owing to their light weight and strong nature the most important application fields of them are the aerospace and transportation industries where structural parts are made of them. The corrosion processes of magnesium alloys, especially when they are in galvanic coupling with other metals are intensively investigated in our days. Scanning electrochemical microscopy is a powerful tool for studying fine details of these processes. The pH, the oxygen concentration, the local concentration of evolved hydrogen as well as local activity of Mg^{2+} ions at the vicinity of the corroding alloy can be mapped with appropriate micro sensor tips. However, the influence of electric field on potentiometric signal, the gas bubble formation, relatively fast changes of the corroding sample surface as well as the interference of pH change on the ion selective magnesium electrode signal makes the SECM measurements challenging task. In our work three barrel micro tip was fabricated and used for studying corrosion of AZ63 magnesium alloy. The tip contained pH measuring antimony barrel, solid contact Mg^{2+} ion selective micropipette and an open pipette that was converted to micro reference electrode employing NaCl internal filling solution and a Ag/AgCl wire as internal reference. The sample-tip distance was set using amperometric approach curves. The electric field distortion during the simultaneous imaging of Mg^{2+} ions and pH distributions could be minimized using the micro-reference electrode. Spontaneous corrosion as well as corrosion under galvanic coupling conditions was studied. The simultaneous measurements confirm that the local pH greatly influences the dissolved Mg^{2+} measurements. A paper has been published about the obtained results¹⁵.

It is expected that evolution of hydrogen gas from corroding magnesium arises from the cathodic half-cell reaction. However, it has been proved that anodized magnesium generates significant amounts of H_2 gas as well. The mechanism resulting in this evolution of hydrogen gas from anodic sites of corroding magnesium is still a puzzle today. In the frame work of the project we started using SECM methods trying to find explanation for it. A new three-step (off-on-off) anodization procedure was worked out and employed in the studies. SECM could be well used for finding the actual sites of hydrogen evolution on anodized Mg alloy surface. Results obtained with combining SECM and scanning vibrating electrode technique (SVET) demonstrated the involvement of catalytic properties of the magnesium-oxide film for the hydrogen-evolution reaction.. In order to evaluate the influence of aluminum, as alloying element on this unexpected hydrogen generation process a model Mg-Al galvanic couple was prepared and scanned in the sample generation-tip collection mode detecting the local hydrogen concentration. SECM experiments were carried out employing anodic polarization on both metals either separated or under galvanic coupling. From our detailed studies no evidence was obtained to sustain the so called noble impurity theory that has been suggested for explanation. In a series of other experiments the hydrogen evolution on 99.9% pure magnesium and on AZ31 magnesium alloy were also compared under various experimental conditions.. Results provided new evidence that the catalytic activity of the $MgO/Mg(OH)_2$ bilayer formed influences the hydrogen evolution rate. The rate of the hydrogen production was enhanced after the formation of the $Mg(OH)_2$ layer on the surface of the metal. Reports about our results have been published in different top journals^{16,17,18}.

2.2.6. Corrosion processes at cut end steel foil coated with Zn and polymer layer

Collaborating with our Spanish colleagues we investigated¹⁹ the distribution of local corrosion processes at the surface of cut edge of a kind of coated steel foil that has widespread technical application. The thin, mild steel foils used for preparation of the samples contained in both side galvanized zinc film and organic polymer layers in order to protect against corrosion. The pieces of the foil were embedded in epoxy resin with their cut end up on the surface and they were soaked in corrosive 0.1 mM NaCl solution. Scanning vibrating electrode technique (SVET) and scanning electrochemical microscopy (SECM) has been employed for the studies. The SVET method could be

used for high resolution mapping of the corrosion processes, while SECM helped to see the chemical nature of the local reactions. For the SECM studies single barrel pH detecting antimony micro-disc electrode and micropipette type ion selective zinc electrodes were prepared. Furthermore novel twisted double barrel micro tip containing antimony micro-disc and ion selective Zn^{2+} micropipette electrode has been developed and used.

2.3. SECM used for studying catalytic activity of chemically modified electrode surfaces

As discussed in the above part of this report, the electro-catalytic activity of corrosion protective surface layers have been investigated in our work with SECM measurements. The methods have been successfully employed in three research areas not related to corrosion studies. In one of them electro-catalytic layer modified composite electrode was developed for electrochemical CO_2 reduction. In the other stable redox mediator film was prepared on carbon electrode surface and a novel method for antioxidant activity assessment has been worked out. While in the third one the characterization of catalytic surface layer of an As measuring electrode has been carried out.

2.3.1. SECM measurements for working out composite electrode for CO_2 reduction

The electrochemical reduction of carbon dioxide to some kind of useful species is a very actively investigated area today. In our work a new electrode optimized for carbon dioxide reduction in the frequently employed capturing medium, aqueous mono-ethanol amine solution, has been developed. The new composite electrode contains nickel coated graphite particles as active matter. During experimental work SECM measurements were employed for detecting the activity of the composite surfaces and for detecting the extent of interfering hydrogen evolution. The SECM method and the results obtained are described in a paper²⁰. The new electrode showed good affinity for carbon dioxide reduction in the medium used. It was revealed that the CO_2 reduction pushes the unwanted hydrogen evolution reaction to more negative values.

2.3.2- Detecting redox mediator activity and stability with SECM

In our work²¹ a novel measuring principle has been introduced for assessing antioxidant activity. The method uses working electrode that is modified with a thin electro-catalytic layer on its surface. Chronopotentiometric detection is employed and the initial slope of electrode potential- time trace is taken as analytical signal. The SECM method could be well used for detecting the activity and stability of different experimental catalyst films immobilized on selected base electrode surface. For understanding the dependence of the analytical signal on different experimental parameters digital simulations were performed using a simplified model²².

2.3.3. Study of gold-crystal violet modified electrode

An electrode for As measurements were prepared by one of our cooperating partner modifying. glassy carbon electrode with nano-size gold-crystal violet film. The modified electrode was characterized in our contribution by scanning electrochemical microscopy (SECM) and electrochemical impedance spectroscopy (EIS).²³

3. Miscellaneous

In the time of the project a new improved version of the SECM apparatus was constructed. In this work new commercial parts like electrochemical workstation and new precision 3D positioning device were used as major units for obtaining better performance. Step by step homemade sample

holder, measuring cells, tip holders etc. were fabricated as well as measuring and evaluating, image making programs were written. The SECM is ready for further applications

Undergraduate students working on their B.Sc or M.Sc. thesis and just in the frame work of scientific undergraduate research (TDK) topics have been taken part in our research aiming to develop and introduce new SECM measuring tips or methods. They learned to use the new chemical microscope, tried out applicability of home written programs. Two Ph.D. dissertation (Mr. Daniel Filotás and Mr. Abdellilah Asserghine) containing results achieved in participating in the project has been written and defended with summa cum laude rate.

We were requested to write a short summary about our SECM work for the Magyar Kémiai Folyóirat. In that paper some of our recent results achieved in the project have been introduced. As far as we know this was the first report appeared in scientific journal written in Hungarian language²⁴.

The second Edition of the basic scientific monograph on SECM edited by A. J. Bard and M. Mirkin has been revised and the third edition has been published. As authors of the chapter of the earlier issues we were ask to bring up to date our chapter, entitled Potentiometric Probes²⁵. In the revised chapter we described several new findings achieved in our work supported by the project.

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